The Ag₂S–Ga₂S₃–As₂S₃ system

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The Ag₂S–Ga₂S₃–As₂S₃ system was investigated by differential thermal and X-ray diffraction. The phase diagrams of the systems Ag₃S–As₂S₃, Ag₆GaS₉–Ag₃AsS₉, AgGaS₂–Ag₃AsS₉, and AgGaS₂–Ag₃AsS₉ were constructed, as well as the liquidus surface projection and the isothermal section at 500 K. The interaction in the Ag₆S–As₂S₃ system is eutectic and is described by the equations L₂1 ↔ Ag₃S + Ag₃AsS₉ (e₁; 25 mol. % As₂S₃, 720 K), L₂2 ↔ Ag₃AsS₂ + Ag₃AsS₉ (e₂; 40 mol. % As₂S₃, 650 K), and L₂3 ↔ Ag₃AsS₉ + As₂S₃ (e₃; 99 mol. % As₂S₃, 580 K). The eutectic point in the AgGaS₂–Ag₃AsS₉ system lies at 94 mol. % Ag₃AsS₉, 653 K. The coordinates of the eutectic in the AgGaS₂–Ag₃AsS₉ system are 92 mol. % Ag₃AsS₉, 670 K, and in the AgGaS₂–Ag₃AsS₉ system the eutectic lies at 90 mol. % Ag₃AsS₉, 687 K.

Phase diagram / Isothermal section / Liquidus surface projection

Introduction

The binary and ternary compounds in the system Ag₂S–Ga₂S₃–As₂S₃ possess non-linear optical, acusto-optical, photoelectric, luminescent, and other properties. The silver thiogallate AgGaS₂ belongs to a class of ternary chalcogenides with the chalcopyrite structure. It exhibits high double refraction and a wide transparency region, and is therefore a promising material for quantum electronics [1]. The ternary compounds Ag₆AsS₉ and Ag₃AsS₉ are used as non-linear optical materials [2,3]. As₂S₃ is a glass-forming compound, and therefore glassy materials should exist in the Ag₂S–Ga₂S₃–As₂S₃ system.

Three compounds, AgGaS₂, Ag₆GaS₉, and AgGaS₂₀S₃₁, form in the Ag₂S–Ga₂S₃ system [4-7]. Ag₆GaS₁₀S₃₁ forms by a peritectic reaction L + Ga₂S₃ ↔ Ag₆GaS₁₀S₃₁ at 1268 K, and has a polymorphous transition at 298 K. AgGaS₂ and Ag₆GaS₉ melt congruently at 1273 K and 1063 K, respectively. AgGaS₂ has a polymorphous transition at 308 K. The phase diagram of the Ag₂S–As₂S₃ system has been investigated in the range 0-50 mol.% As₂S₃ [8]. Two ternary compounds, Ag₁₃AsS₂₃ and AgAsS₂, exist in the system [8-10] and melt congruently at 689 K and 753 K, respectively. According to [11], a glass-formation region was found in the range 100-10 mol.% As₂S₃ of the quasi-binary system Ag₂S–As₂S₃ under the conditions of extremely rapid quenching (cooling rate ~10⁶ K/s).

The phase diagram of the As₂S₃–Ga₆S₉ system was investigated in [12]. No ternary compounds were found, and the sub-solidus region features only the crystallization of the solid solutions of LT-Ga₆S₉ and As₂S₃.

Experimental

High-purity elements (silver 99.999 mass%, gallium 99.997 mass%, sulfur 99.997 mass%) and previously synthesized As₂S₃ (arsenic 99.999 mass%) were used for the synthesis.

All the samples were synthesized in evacuated quartz ampoules with the use of vibration mixing. The temperature in the furnace was raised up to 20-30 K/h to 1100-1200 K. The melts were kept at the maximum temperature for 6 h. The alloys were cooled at the rate of 10-20 K/h to 500 K, and annealed for 600 h to achieve equilibrium state. After annealing, the ampoules were quenched to room temperature into a saturated NaCl solution.

The obtained alloys were investigated by differential thermal analysis (DTA) and X-ray diffraction (XRD). DTA was performed with a set-up consisting of a Thermoden furnace, PDA-1 XY-recorder, and a thermocouple amplifier block. The temperature was controlled by a Pt/Pt-Rh thermocouple. Uniform heating of the furnace was programmed at the rate of 10 K/min, with inertial cooling. Powder diffraction patterns were recorded on...
a DRON 4-13 diffractometer with CuKα-radiation in the 10-80° 2θ range, with 0.05° scan step and 1 s exposure at each point. Powder Cell 2.3 software was used for the X-ray phase analysis.

Results and discussion

As the Ag2S–As2S3 phase diagram had only been investigated in the range 0-50 mol.% As2S3 [8], a re-investigation of the system covering the entire concentration range was performed (Fig. 1). The existence of the two ternary compounds, Ag3AsS3 and AgAsS2, which both melt congruently, was confirmed. The interaction of the components and the ternary compounds is described by the following equations: \( L_1 \leftrightarrow Ag_2S + Ag_3AsS_3 \) (\( e_1 = 25 \) mol.% As2S3, 720 K), \( L_2 \leftrightarrow AgAsS_2 + Ag_3AsS_3 \) (\( e_2 = 40 \) mol.% As2S3, 650 K), and \( L_3 \leftrightarrow AgAsS_2 + As_2S_3 \) (580 K). The temperature of the latter process is only slightly lower than the melting point of As2S3 (583 K), therefore this eutectic is degenerate.

The phase diagram of the AgGaS2–AgAsS2 section was investigated in the entire concentration range (Fig. 2).

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Fig. 1 Phase diagram of the Ag2S–As2S3 system.

Fig. 2 Phase diagram of the AgGaS2–AgAsS2 system.
The results show that the system is of the eutectic type. The coordinates of the eutectic, determined by the construction of a Tamman triangle, are 94 mol.% AgAsS$_3$, 653 K. The solid solubility in the components is negligible.

The phase diagrams of the sections AgGaS$_2$–Ag$_2$AsS$_3$ and Ag$_2$GaS$_3$–Ag$_2$AsS$_3$ are similar, since both of them are of the eutectic type. The eutectic coordinates are 92 mol.% Ag$_2$AsS$_3$, 670 K for the AgGaS$_2$–Ag$_2$AsS$_3$ system, and 90 mol.% Ag$_2$AsS$_3$, 687 K for the Ag$_2$GaS$_3$–Ag$_2$AsS$_3$ system.

The liquidus surface projection of the Ag$_2$S–Ag$_2$S$_3$–As$_2$S$_3$ system consists of five sub-systems: Ag$_2$S–Ag$_2$GaS$_3$–Ag$_3$AsS$_3$, Ag$_2$GaS$_3$–Ag$_2$AsS$_3$, AgGaS$_2$–Ag$_2$AsS$_3$, AgGaS$_2$–AgAsS$_3$, AgGaS$_2$–Ga$_2$S$_3$–As$_2$S$_3$, and AgGaS$_2$–Ga$_2$S$_3$–As$_2$S$_3$, which may be viewed as independent.

The liquidus of the four sub-systems (except AgGaS$_2$–Ga$_2$S$_3$–As$_2$S$_3$) consists of the three curves of primary crystallization of the components that form the sub-system. The liquidus of the AgGaS$_2$–Ga$_2$S$_3$–As$_2$S$_3$ system consists of five fields of primary crystallization of AgGaS$_2$, α-Ga$_2$S$_3$, β-Ga$_2$S$_3$, Ag$_2$Ga$_2$S$_3$, and As$_2$S$_3$. The temperature of the ternary eutectic E$_5$ in the AgGaS$_2$–AgAsS$_3$–As$_2$S$_3$ sub-system is 577 K, which differs only insignificantly from the eutectics in the systems AgAsS$_3$–As$_2$S$_3$ (580 K), AgGaS$_2$–As$_2$S$_3$ (582 K), and slightly more from that of the system AgGaS$_2$–AgAsS$_3$ (653 K). Analogous situations are observed for the non-variant points E$_4$ and P$_2$. The As$_2$S$_3$ content of the non-variant points E$_4$, E$_5$, P$_2$ is 98 mol.% As$_2$S$_3$, which complicates the preparation of crystalline samples of this composition and hence the investigation of the phase diagram in this part of the system (see enlargement in Fig. 5).

Fig. 3 Phase diagram of the Ag$_2$Ga$_2$S$_3$–As$_2$S$_3$ system.

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Fig. 4 Isothermal section of the Ag$_2$S–Ga$_2$S$_3$–As$_2$S$_3$ system at 500 K.

Fig. 5 Liquidus surface projection of the Ag$_2$S–Ga$_2$S$_3$–As$_2$S$_3$ system.
Conclusions

Based on the results of X-ray diffraction and differential thermal analysis, we investigated the phase diagrams of the systems Ag₂S–As₂S₃, Ag₄GaS₆–Ag₃AsS₃, AgAsS₂–AgGaS₂, and AgGaS₂–Ag₃AsS₃, as well as the liquidus surface projection and the isothermal section at 500 K of the Ag₂S–Ga₂S₃–As₂S₃ system. The nature and temperature of the non-variant and monovariant processes were determined.

References